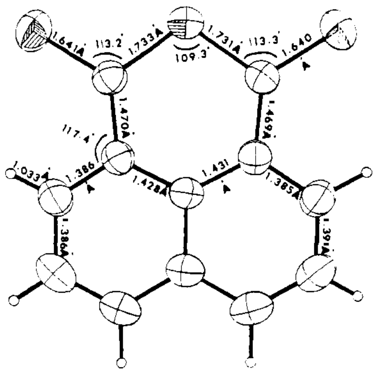


Figure 1. X-ray crystal structure of thioanhydride **8**.

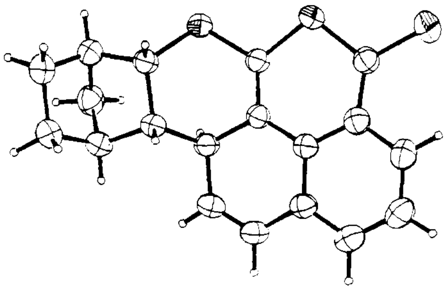
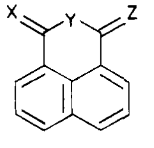
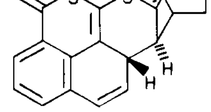


Figure 2. X-ray crystal structure of cycloadduct **9**.

showed no carbonyl absorption; attempts to introduce a third sulfur into **6** using reagent **5** failed. Dithione **6** was rearranged rapidly (90%) by a catalytic amount of triethylamine in cold DMF to the isomeric thionothioanhydride **7**, which formed green needles, mp 205 °C dec.[6] Thionation of isomer **7** by reagent **5** in boiling chlorobenzene (40 min, N_2) occurred smoothly to give (65%) the trithioanhydride **8** as black irridescent needles, mp 225 °C[7] dec, which were extremely stable, both in the solid state and in refluxing neutral organic solvents like ethanol, benzene, acetonitrile, and chlorobenzene. A single-crystal X-ray analysis of trithioanhydride **8** was carried out[7] (Figure 1).



6. X = Z = S, Y = O
7. X = Y = S, Z = O
8. X = Y = Z = S



9

Compound **8** underwent a novel nonphotochemical addition to norbornene under remarkably mild conditions (15 min in refluxing MeCN or overnight at room temperature). The resulting bright red 1:1 adduct, mp 170 °C, was found to have structure **9**,[11] as determined by X-ray crystallography (Figure 2). The formation of this adduct may be viewed as involving an inverse demand (2 + 4) cycloaddition of the norbornene olefinic bond to an electron-deficient ene–thione moiety of the aromatic thioanhydride system. The closest analogy to this unusual reaction appears to be found in the diene type behavior of the α-dithione function of dimethyl tetrathiooxalate.[12]

Further aspects of the chemistry of cyclic thioanhydrides are currently under investigation in our laboratories.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 83-03897).

Registry No. 4, 91384-89-3; **6**, 91384-90-6; **7**, 91384-91-7; **8**, 91384-92-8; **9**, 91384-93-9; norbornene, 498-66-8.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(6) Mass spectrum of **7**: *m/e* 230 (100%, M^+), 202 (83%, M – 28), 186 (35%, M – 44), 170 (47%, M – 60), 158 (28%, M – 28 – 44), 154 (15%, M – 76), 126 (50%, M – 60 – 44). NMR spectrum: δ 9.02 (dd, J = 7.5, 1.25 Hz, 1 H), 8.60 (dd, J = 7.5, 1.25 Hz, 1 H), 8.32 (dd, J = 6, 1.25 Hz, 1 H), 8.28 (dd, J = 6, 1.25 Hz, 1 H) 7.76 (t, J = 8.0 Hz, 1 H), 7.72 (*t*, J = 8.0 Hz, 1 H). UV–vis: $\lambda_{max}{}^{C_2H_4Cl_2}$ 252 nm (log ϵ 4.34), 273 sh (4.06), 322 sh (4.00), 335 (4.06), 375 sh (4.08), 410 (4.27); $\lambda_{max}{}^{CS_2}$ 532 sh (1.72), 566 (1.81), 600 (1.81), 640 (1.66). Rearrangement of **6** to **7** appears to also occur readily under electron impact, as evidenced by a strong M – 28 peak in the mass spectra of **6** as well as **7**.

(7) Mass Spectrum of **8**: *m/e* 246 (100%, M^+), 202 (33%, M – 44), 170 (45%, M – 76), 126 (35%, M – 44 – 76). NMR spectrum: δ 8.88 (dd, J = 7.5, 1.25 Hz, 2 H), 8.26 (J = 7.5, 1.25 Hz, 2 H), 7.68 (t, J = 7.5 Hz, 2 H). UV–vis spectrum: $\lambda_{max}{}^{C_2H_4Cl_2}$ 250 nm, sh (log ϵ 4.11), 265 (4.29), 360 infl (4.04), 375 (4.04), 379 sh (4.01), 443 (4.36), 523 br (2.79), 553 (2.81); $\lambda_{max}{}^{CS_2}$ 533 (2.55), 562 (2.66), 633 br (1.94), 681 (1.92). The planar molecules form stacks parallel to the *c*-axis with the S=C—S—C=S moiety sandwiched between the naphthalene units along the stacks. There are no unusual intermolecular contacts. The distortion of the naphthalene unit is small and not dissimilar to that observed in other 1,8-disubstituted naphthalenes.[8] The C=S bond lengths (1.640 and 1.651 Å) are similar to that reported for thiobenzophenone (1.636 (9) Å).[9] The C–S bond lengths (1.731 and 1.733 Å) are similar to that found for simple diaryl sulfides (1.75 Å),[10] indicating no appreciable mesomeric polarization in the thioanhydride function (Figure 1).

(8) Schweizer, W. B.; Procter, G.; Kaftory, M.; Dunitz, J. *Helv. Chim. Acta*. **1978**, *61*, 2783.

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(11) Mass spectrum of adduct **9**: *m/e* 340 (22%, M^+), 246 (100%, M – 94), 202 (30%, M – 94 – 44), 170 (24%, M – 94 – 76). NMR spectrum: δ 8.80 (m, 1 H), 7.50 (m, 2 H), 6.70 (m, 1 H), 6.40 (m, 1 H), 3.15 (m, 1 H), 2.70 (br, 1 H), 2.60 (m, 1 H), 2.35 (m, 1 H), 2.20 (m, 1 H), 1.6–1.8 (m, 3 H), 1.1–1.4 (m, 3 H). Norbornadiene adduct **9** crystallizes in the monoclinic space group $P2_1/c$. Cell dimensions: a = 10.612 (1) Å, b = 14.266 (1) Å, c = 11.153 (2) Å, β = 110.43 (1)°, Z = 4, d_{calcd} = 1.430 g cm^{-3}. R = 0.047 (R_w = 0.059), 263 parameters refined with 2349 reflections ($I > 3\sigma$).

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Acid-Catalyzed Intramolecular "Diels-Alder" Reactions. The Cycloaddition of Allyl Cations to 1,3-Dienes

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During the last decade, extensive activity has existed in the study of intramolecular Diels–Alder reactions, especially as exploited in the synthesis of natural products.[2] A major limitation of this intramolecular 2 + 4 cycloaddition reaction is that activating groups have to be built into the dienophile in order to achieve the desired reactivity.[3] Because of our extensive interest in carbocations[4] and cation radicals,[5] we were intrigued by the possibility

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(1) National Science Foundation Fellow 1983–1984.

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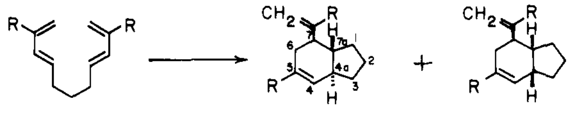
Table I. Catalysis of the Cyclization of **2** with Aminium Cation Radical and with Protic Acids

catalyst	time, min	temp, °C	% yield[a]		
			4	**5**	**8**
6	20	−23	64	15	14
$HSbCl_6$[b,c]	1	−23	64	17	13
CF_3SO_3H[b]	3	−23	65	23	3
p-$CH_3C_6H_4SO_3H$[b]	90	25	74	12	8

[a] Yields were determined by HPLC analysis vs. tetradecane as an internal standard. [b] The protic acids were used in 10 mol % relative to **2**. The concentration of **2** was 0.005 M in methylene chloride. [c] Solutions of $HSbCl_6$ were prepared by bubbling dry hydrogen chloride gas into ~0.1 M $SbCl_5$ in 1,1,2-trichlorotrifluoroethane at −30 °C under an inert atmosphere.

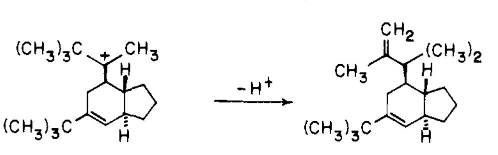
of applying cationic cyclization and the "cation radical catalyzed Diels–Alder reaction"[6] to the intramolecular 2 + 4 cycloaddition of unactivated polyene systems. We now wish to report that such intramolecular cycloadditions can be accomplished with either protic acid or aminium cation radical catalysts in high yield with high stereospecificity. In addition, we found that, in some systems, the aminium cation radical appears to act mainly as an indirect source of protons, which are then utilized in an acid-catalyzed cyclization.

In order to study the catalyzed formal intramolecular "Diels–Alder" reaction of unactivated systems, we prepared **1**–**3**.[7,9] Refluxing of **1** in xylene (bp 140 °C) for 48 h gave no cycloaddition product, while similar thermal treatment of **2** gave 63% of a 2:1 mixture of **4** and **5**, respectively.[9] In contrast to the relatively unreactive nature of **1** under the described thermal conditions, treatment of **1** with 20 mol % of tris(*p*-bromophenyl)aminium hexachloroantimonate (**6**)[10] at −12 °C for 20 min gave 42% of **7** (98% purity) as the only monomeric product. Similar treatment of **2** with 10 mol % of **6** at −23 °C gave 64% of **4**, 15% of **5**, and 14% of **8**. The formation of **8** suggested the presence of a cationic intermediate such as **9**, which would not be expected from a cation radical catalyzed cyclization.[11] When **3**, the cis–trans isomer of **2**, was treated with 10 mole % of **6**, we obtained 28% of **4**, 33% of **5**, and very small amounts of **8**.



1 R = CH_3 **7** R = CH_3

2 R = $C(CH_3)_3$ **4** R = $C(CH_3)_3$ **5** R = $C(CH_3)_3$

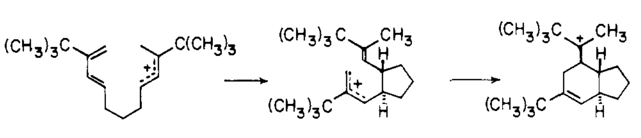


9 **8**

The formation of **4** from **3** was mechanistically significant, since this unusual example of a cis olefin in a diene leading to a *trans*-perhydroindene skeleton precludes a concerted cyclization.[11,12] In view of the observations noted above, we explored the reaction of **2** with **6** in more detail. It was found that (a) this reaction showed an induction period at −30 °C, (b) this induction period was significantly increased in base washed glassware, and (c) 2,6-di-*tert*-butylpyridine, which does not react with **6**, completely inhibited the reaction of **2** with **6**. These results, and the formation of **8**, were more consistent with a proton-catalyzed process than with an electron-transfer process.[13]

In order to test these concepts, **1** was treated with 4 mol % of trifluoromethanesulfonic acid in methylene chloride at −23 °C. *After 6-min reaction time, an 88% yield of 7 was obtained.*

Similarly, treatment of **2** with various protic acids gave the results shown in Table I. These results are consistent with the initial protonation of **2** to produce the allylic cation **10**. Intramolecular cycloaddition of the allylic cation to the diene would produce the new allylic cation **11**, which could then yield **9**.[16] Loss of a proton from **9** would give **4** and **5**, while rearrangement followed by proton loss would lead to **8**. As shown in Table I, both the rate of the reaction and the product ratios appeared to be somewhat dependent on the proton source. Thus, the counterion would appear to be implicated in a minor way. Catalysis by strong acids such as trifluoromethanesulfonic acid is generally preferred.



10 **11** **9**

In summary, we have demonstrated that intramolecular cyclizations of tetraenes can be accomplished via acid catalysis.[17] We believe that this involves the initial intramolecular addition of an allylic cation to the diene. We are continuing to explore both the synthetic and mechanistic aspects of these findings.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE81-14772, which supported this investigation.

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(7) Treatment of glutaraldehyde with the ylide derived from methallyltriphenylphosphonium chloride[8] and with the ylide obtained from 2-*tert*-butylallyltriphenylphosphonium bromide[9] gave *trans*,*trans*-2,10-dimethyl-1,3,8,10-undecatetraene (**1**, 28%) and *cis*,*trans*-2,10-dimethyl-1,3,8,10-undecatetraene (11%), and *trans*,*trans*-2,10-di-*tert*-butyl-1,3,8,10-undecatetraene (**2**, 23%) and *cis*,*trans*-2,10-di-*tert*-butyl-1,3,8,10-undecatetraene (**3**, 10%), respectively.

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(9) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds. In all cases, NMR and IR spectral data were consistent with the assigned structures. The stereochemistry of **4**, **5**, and **7** was assigned from H_7–H_{7a} coupling constants of 10.9, 11.2, and 10.9 Hz, and H_{4a}–H_{7a} coupling constants of 10.9, 7.7, and 10.9 Hz, respectively, which were obtained by decoupling experiments at 300 MHz. The stereochemistry of **8** was assigned from an H_{4a}–H_{7a} coupling constant of 11.0 Hz and the presence of identical splitting patterns for the H_{4a}, H_4, and H_6 protons in **8** and **4**.

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(11) Compounds **4**, **5**, and **8** were not interconverted under the reaction conditions. Similarly, **2** and **3** were not interconverted under the reaction conditions.

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(17) In an attempt to apply this intramolecular cyclization to an intermolecular case, we studied the acid-catalyzed behavior of 1,3-cyclohexadiene. While we could reproduce the literature results[6] with **6**, only trace amounts of Diels–Alder dimers could be obtained with protic acids.